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Growth and characterisation of potassium dihydrogen phosphate (KDP) crystal doped with amino acids

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Abstract · Pure and amino acid doped potassium dihydrogen phosphate (KDP) crystals have been grown by solution technique at room temperature The powder X – ray diffraction studies for the grown crystals have been made. The dielectric behaviour of the pure and doped crystals has been studied in the microwave region using K – band microwave bench equipped with the Gunn oscillator and guided with rectangular wave guide The grown crystals are subjected to Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC), in order to identify the changes in the thermal stability and structural phase transitions.

Keywords Growth of KDP crystals, doping effect, amino acids

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1. Introduction

Ferroelectric potassium dihydrogen phosphate (KDP) crystals are widely used in modern short wavelength laser techniques, nonlinear and integrated optics. These crystals are applied as three-dimensional electro-optical devices, solid optical media for the frequency transformation of coherent radiation (generators of harmonics, generators of sum and difference frequencies for high power laser radiation, optical parametric oscillators for the infra-red spectral range) and integrated optical waveguides. They are also used as Q - switches and shutters for high-speed photography. KDP is characterized by high nonlinear performance, wide optical transparency range and well-developed technology of growth. The point group of the crystal is $42m$ and the space group is $I\bar{4}\,2d$ (122). The structure belongs to the scalenohedral (twelve face polyhedron) class of tetragonal system.

Organic crystals [1 - 3] possess high efficiency of frequency conversion, high damage threshold, wide range of transparency. In spite of having all positive factors, the organic crystals could not be employed satisfactorily, because of their poor mechanical and thermal stability. So, semi organic crystals which have combined properties of both inorganic and organic species, are expected to have good optical, thermal and mechanical properties. KDP crystals doped with ionic impurities have better, nonlinear optical property than pure KDP crystals. Some of the amino acids like alanine, leucine, histidine *etc.*, are good nonlinear optical materials but the growth of large-sized defect-free crystals is difficult. In the present work, the properties of KDP crystal doped with amino acids, namely, α - alanine, β - alanine, α - leucine, α - histidine, α - cystine and α - valine have been investigated through powder XRD, FTIR, FTRaman and thermal analyses along with dielectric properties in the microwave region. The zwitter ion present in the amino acids when mixed with pure KDP crystal, alters the characteristics of the pure crystal.

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2. Experimental

2.1 Growth of the crystal :

The pure and doped KDP crystals were grown using solution growth technique. Recrystallised salts of KDP (99 % purity) and triple-distilled water were used in the present crystal growth experiment. Saturated solutions of KDP (each 250 ml) are separately mixed with 0.1 M solutions of the above amino acids (99% purity) and stirred well using a stirrer. The well-mixed solutions are allowed to evaporate at room temperature. Good-

sized crystals were grown within two weeks and the photographs of the grown crystals are presented in Figure 1.

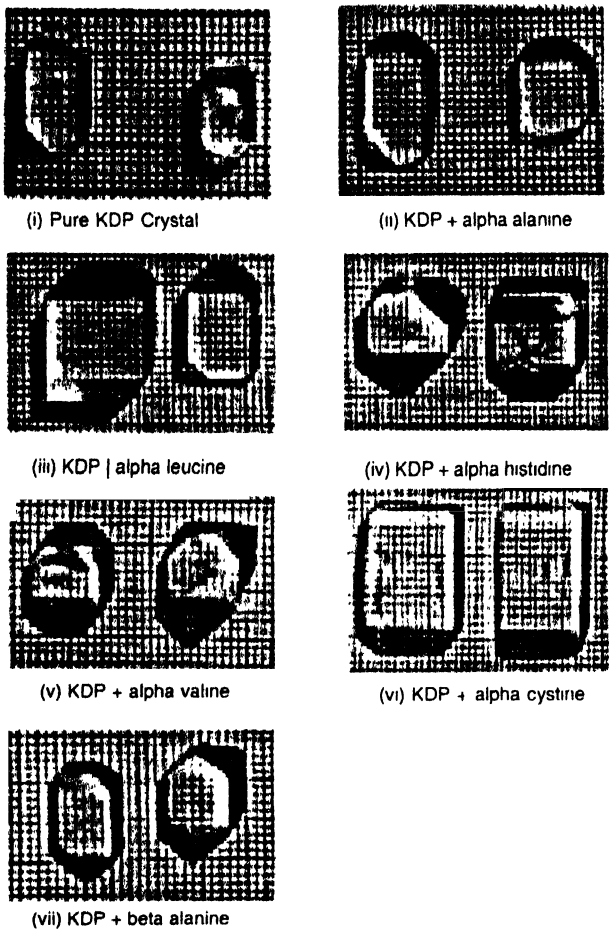


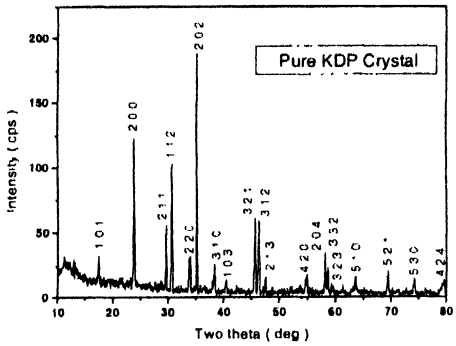
Figure 1. Photographs of pure and amino acids-doped KDP crystals.

2.2 Instrumentation :

The powder XRD data for the crystals were recorded on high resolution GUINER X - Ray Diffractometer (SEIFERT, Germany). The indexed powder XRD patterns for pure KDP and doped crystals are presented in the Figure 2.

The FTIR and FT Raman Spectra of the crystals were recorded on BRUKER IFS 66V Spectrophotometer in the regions of 4000 – 400 cm^{-1} and 3500 - 50 cm^{-1} respectively and are presented in the Figures 3 (a) and 3 (b) respectively. The microwave bench operating at K- band frequencies with Gunn diode as the microwave source was used to determine the dielectric constant of the samples. The dimension of the waveguide used in the present case is 1.1 cm × 0.4 cm and hence the crystals are shaped according to this size.

The thermal analysis of the crystal has been carried in the presence of nitrogen atmosphere at a scanning rate of 20 °C per minute using PERKIN – ELMER thermal analysis instrument. The TGA was carried out in the temperature range of 50 °C



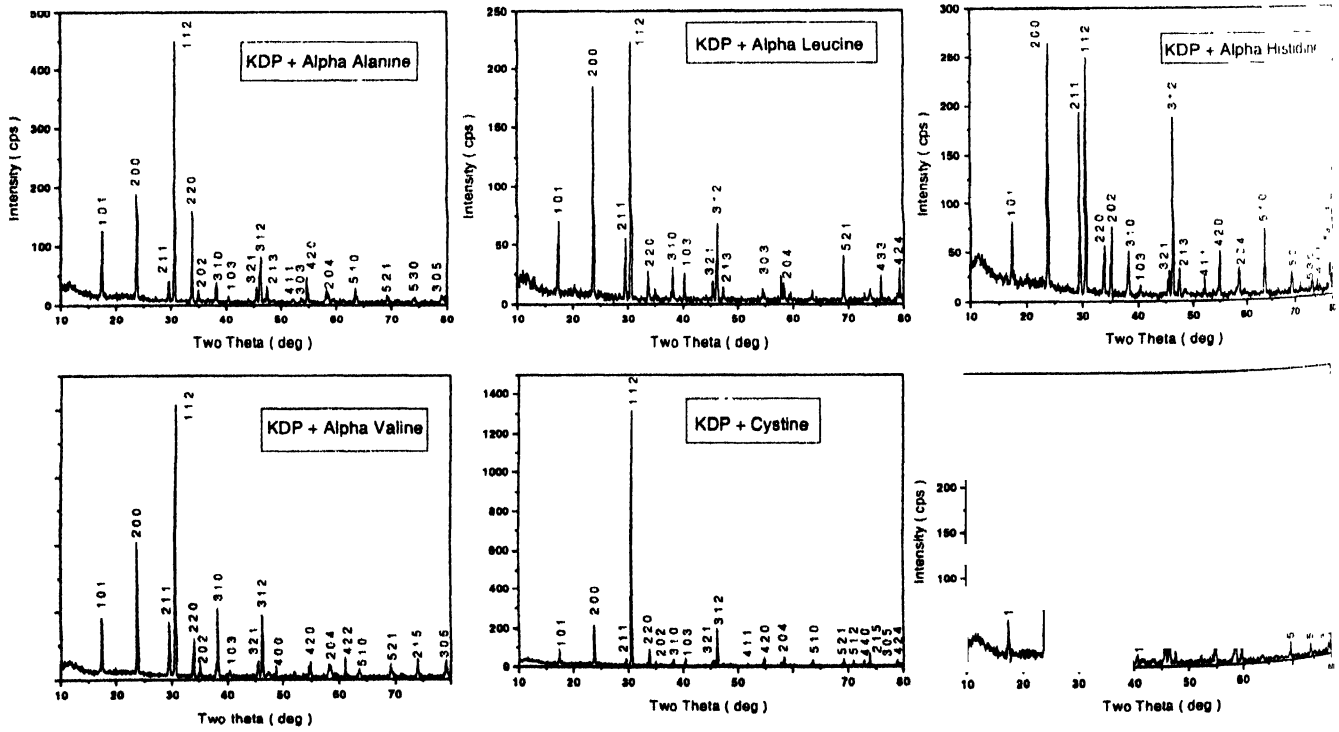


Figure 2. Indexed powder XRD pattern for pure and amino acid-doped KDP crystals.

800°C and DSC was carried out in the temperature range 50°C–400°C. The TGA and DSC curves for the pure and doped crystals are presented in the Figure 4.

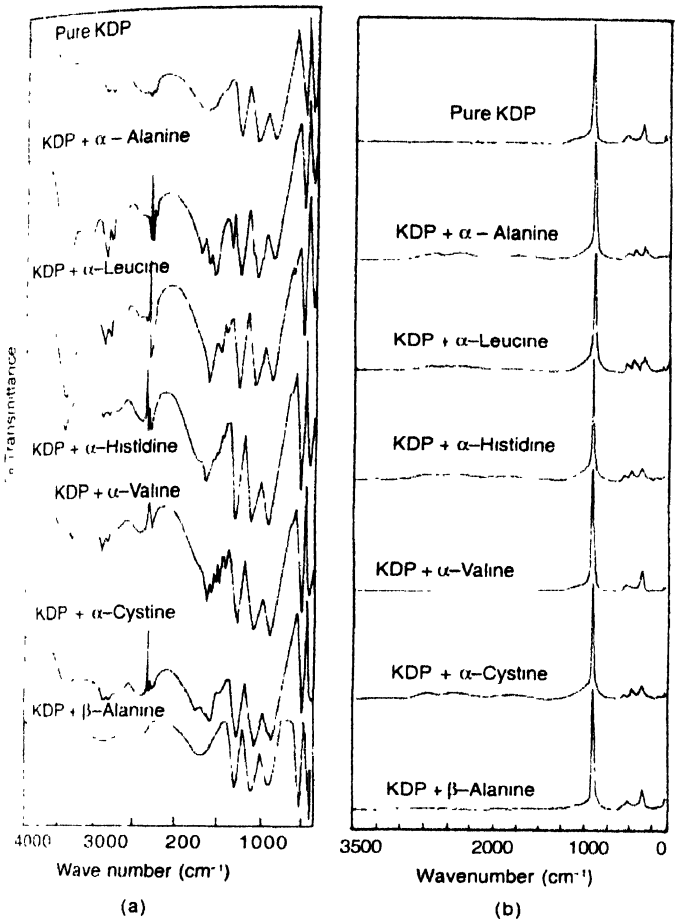


Figure 3. FTIR and FTRaman spectra of pure and amino acid-doped KDP crystals

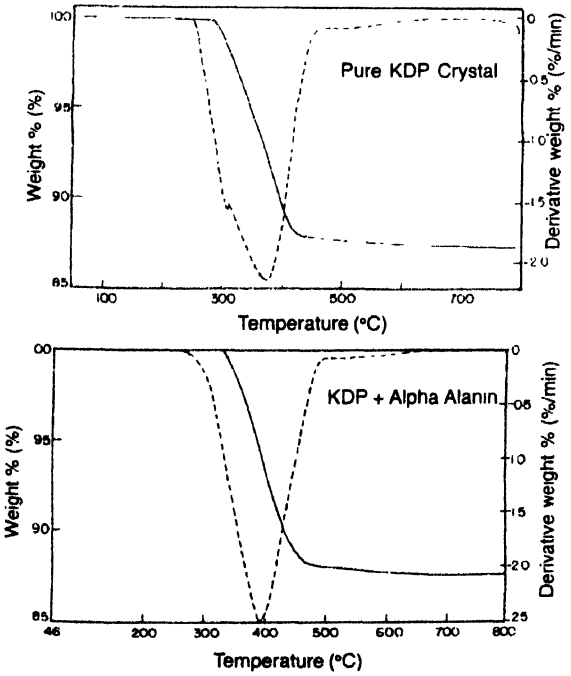
3. Results and Discussion

3.1 X - Ray diffraction analysis :

The presences of impurity in the doped crystals are confirmed by powder X-ray diffraction. The XRD pattern for the pure KDP [2, 4] is compared with the standard values of KDP and is in agreement with it. From the powder XRD data, the various Bragg's reflections were indexed using Joint Committee on Powder Diffraction Standards (JCPDS) values for the pure and doped crystals. The indexed data for the pure and doped KDP crystals are presented in the Tables (1 - 7). By using UNIT CELL Software program, the lattice parameters for the crystals have been calculated and are presented in Table 8. The deviation of 2θ values, the variations of intensity of various Bragg's reflections and hence in the lattice parameters, are due to the incorporation of the dopants and causes the lattice contraction for all the doped crystals.

3.2 Vibrational band analysis :

The structural investigations for the KDP [5-12] and its isomorphous crystals like ammonium dihydrogen phosphate, cesium dihydrogen phosphate, rubidium dihydrogen phosphate *etc.*, have been carried out by several researchers through FTIR and FTRaman techniques. The atomic arrangements in KDP [13] are such that each P-atom is surrounded by four O-atoms, at the corners of a regular tetrahedron. Each PO_4 group is linked with four other PO_4 groups by H-bond. Neutron diffraction studies revealed that each PO_4 group has two nearest hydrogen and as a group, they form $[H_2PO_4]^-$ ion. The PO_4 group and the K ions are built-up in such a way that K and P atoms alternate each other at a distance of $c/2$ along the c - axis. Each K ion is surrounded by eight O's and four of them are nearer than the other four.



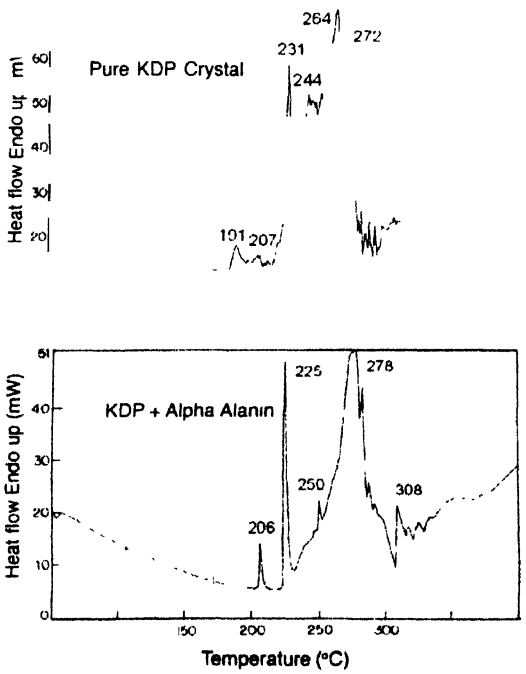


Fig. 4 contd

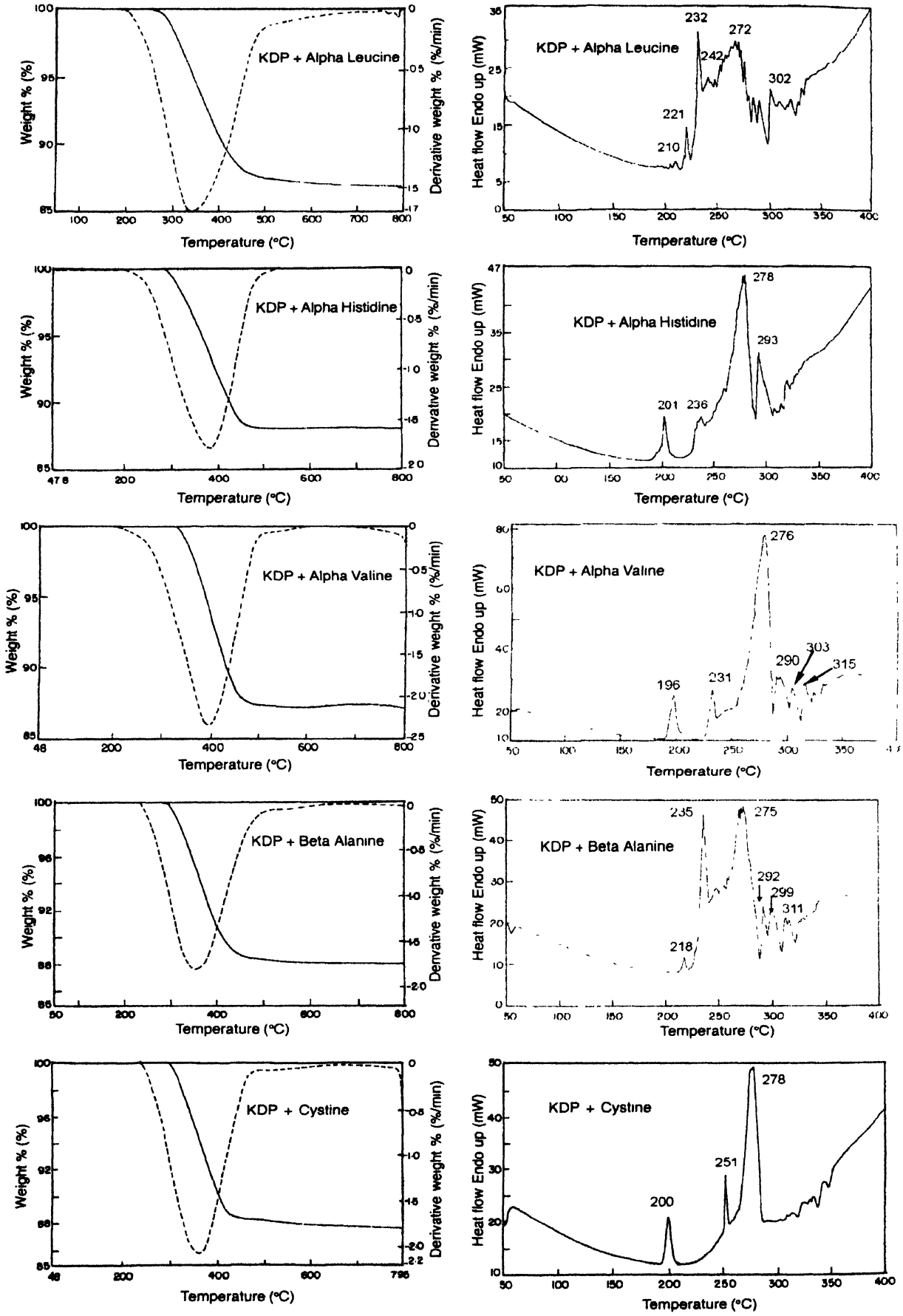


Figure 4. TGA and DSC curves for pure and amino acid-doped KDP crystals.

ible 1. Indexed XRD data for pure KDP crystal.

No	*h*	*k*	*l*	*d*(obs)	*d*(calc)	Diff. (*d*)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5.09252	5.10635	-0.01383	17.400	17.353	0.047
2	2	0	0	3.73173	3.72595	0.00578	23.825	23.863	-0.037
3	2	1	1	3.01189	3.00987	0.00202	29 636	29.657	-0.020
4	1	1	2	2 91528	2.91868	-0.00340	30.642	30.606	0.037
5	2	2	0	2.63824	2.63465	0 00359	33.952	34 000	-0 048
6	2	0	2	2.55069	2.55317	-0.00248	35 155	35 120	0 035
7	3	1	0	2.34623	2.35650	-0.01027	38.333	38.159	0 174
8	1	0	3	2.22979	2 22996	-0 00017	40.420	40 416	0.003
9	3	2	1	1 98980	1.98244	0 00736	45.551	45 730	-0 179
0	3	1	2	1.96024	1 95570	0.00454	46.278	46.391	-0.114
1	2	1	3	1.91292	1.91345	-0.00053	47.492	47.478	0.014
2	4	2	0	1 67108	1.66630	0.00478	54.898	55 069	-0.171
3	2	0	4	1 58589	1 58606	-0.00017	58 119	58 113	0 007
4	3	3	2	1.57318	1.57035	0.00283	58.634	58 751	-0 116
5	3	2	3	1 55667	1.54822	0 00845	59 318	59.675	-0 357
6	5	1	0	1.46261	1.46144	0.00117	63 560	63.617	-0.057
7	5	2	1	1.35263	1 35759	-0.00496	69 428	69.138	0 290
8	5	3	0	1.27698	1.27799	-0 00101	74 202	74 133	0.069
9	4	2	4	1 20468	1 20767	-0 00299	79 497	79 262	0 236

ble 2. Indexed XRD data for α - alanine doped KDP crystal

No	*h*	*k*	*l*	*d*(obs)	*d*(calc)	Diff. (*d*)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5 07785	5 09670	-0 01885	17 451	17 386	0 065
2	2	0	0	3.73755	3 73206	0.00549	23 787	23 823	-0.036
3	2	1	1	3 02166	3 01111	0 01055	29 538	29.644	-0 106
4	1	1	2	2 91238	2 91003	0 00235	30.673	30 699	-0 025
5	2	2	0	2.64924	2.63896	0.01028	33 807	33 943	-0.136
6	2	0	2	2 56283	2 54835	0.01448	34 983	35 188	-0 205
7	3	1	0	2 35214	2.36036	-0 00822	38 233	38.095	0.138
8	1	0	3	2.22892	2 22016	0.00876	40 436	40 602	-0 167
9	3	2	1	1.98930	1.98464	0.00466	45 563	45 677	-0.113
0	3	1	2	1.95848	1.95485	0.00363	46.322	46 413	-0 091
1	2	1	3	1.91383	1.90806	0.00577	47.468	47 620	-0 152
2	4	1	1	1.75159	1.75228	-0 00069	52 179	52 157	0 022
3	3	0	3	1.70691	1.69890	0 00801	53.652	53 925	-0.273
4	4	2	0	1.67587	1.66903	0.00684	54.728	54 971	-0.243
5	2	0	4	1.58350	1.58004	0.00346	58.215	58 355	-0.140
6	5	1	0	1.46399	1.46383	0 00016	63 493	63.501	-0.008
7	5	2	1	1.35618	1.35948	-0.00330	69.221	69.029	0.192
8	5	3	0	1.27750	1.28009	-0.00259	74.166	73 992	0 175
9	3	0	5	1.21095	1 21696	-0.00601	79.005	78.539	0.465

The skeletal bending vibrations of $[H_2PO_4]^-$ ion usually occurs in the region of 300 – 600 cm^{-1} [17]. The strong bands observed in the FTIR spectrum of pure KDP crystal at 403, 417, 426, 439, 458 and 534 cm^{-1}, are attributed to OPO bending vibrations. The band at 364, 529 and 534 cm^{-1} with weak intensity in the FTRaman spectrum of the pure crystal, are also due to OPO bending vibrations. The bands observed in the region of 900–1400 cm^{-1} belong to the skeletal stretching vibrations of the dihydrogen phosphate ion. As expected, the very strong bands appear at 905 and 916 cm^{-1} in the FTIR and FTRaman spectra are due to the OPO symmetric stretching. The corresponding asymmetric vibrations appear at 1099 and 1300 cm^{-1} with strong intensity in the FTIR spectrum. The strong band observed at 1622 cm^{-1} is due to HOH bending. The band at 2363 cm^{-1} with medium intensity is due to OH symmetric stretching vibration. The OH asymmetric stretching vibrations appear at 2835, 2921 and 3400 cm^{-1}. All the bands observed in the Raman spectra of the pure and doped crystal below 300 cm^{-1}, might be due to lattice vibrations.

In the spectra of amino acids-doped crystals, some of the bands of $[H_2PO_4]^-$ ion overlap with the amino acid vibrations and hence, intensity of the bands increases. Few bands of dihydrogen phosphate ion become broader due to overlapping. Also some of the frequencies are slightly shifted.

In the amino acid-doped crystals, the vibrations of NH_3^+ ion of amino acid [14 - 16] appear in the FTIR and FTRaman spectra of all the crystals. The asymmetric stretching vibrations of NH_3^+ ion appear in the region of 3090–3400 cm^{-1} with strong and medium intensities. Some of them overlap with the OH stretching vibrations of dihydrogen phosphate ion. The asymmetric deformations of NH_3^+ ion appear in the valine and cystine-doped crystals at 1659 and 1669 cm^{-1} with strong intensity respectively. The symmetry deformation of NH_3^+ ion appears at around 1500 cm^{-1} in all the spectra of all the doped crystals with medium intensity. The strong intensity bands at around 1602 cm^{-1} in the FTIR spectra of doped crystals is due to COO - asymmetric stretching vibrations of amino acid. The band at 1400 cm^{-1} in the FTIR spectrum of α – alanine-doped crystal is due to COO^- symmetric stretching vibration. The wagging vibrations of COO^- ion usually appear at a frequency of 560 cm^{-1}. As expected, this band appears in the FTRaman spectrum of doped crystal

Table 3. Indexed powder XRD data for α - leucine doped KDP crystal.

S.No	h	k	l	d(obs)	d(calc)	Diff (d)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5 10598	5 09914	0 00684	17 354	17.377	-0.023
2	2	0	0	3.74299	3.72970	0.01329	23.752	23.838	-0 086
3	2	1	1	3.02245	3 01037	0 01208	29.530	29.652	-0.121
4	1	1	2	2 92762	2.91240	0.01522	30.510	30.673	-0.163
5	2	2	0	2.65854	2.63730	0.02124	33 685	33 965	-0 280
6	3	1	0	2 35425	2 35887	-0 00462	38.197	38.120	0.078
7	1	0	3	2.23826	2.22297	0.01529	40.260	40.549	-0 289
8	3	2	1	1.99349	1.98372	0.00977	45.462	45.699	-0.237
9	3	1	2	1.96189	1 95489	0 00700	46 237	46.412	-0 175
10	2	1	3	1.91840	1.90953	0 00887	47 348	47.582	-0 234
11	3	0	3	1.68029	1.69971	-0 01942	54 572	53.898	0.674
12	2	0	4	1.57951	1.58174	-0 00223	58.377	58 286	0.090
13	5	2	1	1.35769	1 35873	-0.00104	69.133	69 072	0 060
15	4	3	3	1 25237	1 25621	-0 00384	75 914	75 641	0.273
16	4	2	4	1.20788	1.20627	0.00161	79.245	79 372	-0 127

Table 4. Indexed powder XRD pattern for α- histidine doped KDP crystal

S.No	h	k	l	d(obs)	d(calc)	Diff (d)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5.11332	5.09130	0.02202	17.329	17 404	-0 076
2	2	0	0	3 73898	3 73267	0.00631	23 778	23 819	-0.041
3	2	1	1	3.03249	3.01031	0.02218	29.430	29 652	-0.222
4	1	1	2	2.92198	2 90587	0.01611	30.570	30 744	-0 174
5	2	2	0	2.64329	2.63939	0.00390	33 886	33.937	-0.052
6	2	0	2	2.54946	2.54565	0.00381	35.173	35.227	-0.054
7	3	1	0	2.35031	2.36075	-0.01044	38.264	38.088	0 176
8	1	0	3	2.23146	2 21590	0 01556	40 388	40.684	-0 296
9	3	2	1	1 98730	1.98459	0 00271	45.612	45.678	-0.066
10	3	1	2	1.95800	1.95376	0.00424	46.334	46.440	-0 106
11	2	1	3	1.91278	1.90543	0.00735	47.496	47.690	-0 194
12	4	1	1	1.75328	1.75231	0.00097	52.124	52.156	-0.031
13	4	2	0	1 67260	1 66930	0.00330	54.844	54.961	-0.118
14	2	0	4	1 57561	1.57733	-0 00172	58.535	58.465	0.070
15	5	1	0	1.46494	1.46407	0.00087	63.447	63.489	-0.042
16	5	2	1	1.35651	1.35958	-0.00307	69.201	69.023	0.179
17	5	3	0	1.27797	1.28029	-0.00232	74.135	73.977	0.157
18	4	3	3	1.25867	1.25561	0.00306	75.468	75.684	-0.216
19	3	0	5	1.21081	1.21504	-0.00423	79.016	78.688	0.328
20	4	2	4	1.20336	1.20471	-0.00135	79.602	79.495	0.107

and also this band overlaps with the OPO bending vibrations of dihydrogen phosphate ion. The CH bending vibrations of amino acids appear at a frequency of 1447 cm^{-1} in the FTIR spectra of valine, leucine and histidine doped KDP crystals. In the FTIR spectrum of valine doped crystal, a strong band appears at 1559 cm^{-1}. This is due to C = O symmetric stretching vibrations of amino acids. In the FTRaman spectrum of cystine–doped KDP crystal, the weak band at 1830 cm^{-1} is attributed to SH vibration [14]. The above mentioned bands in the FTIR and FTRaman spectra of doped crystals confirm the presence of amino acids in the doped crystals.

3.3 Dielectric studies :

Using a K-band microwave test bench, microwave measurements have been carried out to determine the dielectric constants of the pure and doped KDP crystals. A direct and accurate method of Robert and Von - Hipple [18] was used to measure the dielectric constant of the samples. The c axis of the KDP crystal have been identified and the crystals are cut perpendicular to c - axis and are shaped in order to suit the waveguide. The Von Hipple method is based on the measurement of shift in the minimum of standing wave produced by a short circuit when a sample of dielectric is placed in front of the short circuit. The shift 'Δ' in the minimum of standing wave is caused due to the presence of the samples. From the shift, the dielectric constant of the pure and doped KDP crystals have been calculated at a frequency of 19.403 GHz and presented in Table 9. The dielectric constant (ε_r) of the crystals is evaluated by using,

$$\beta_d = 2\pi/\lambda_0\left[\varepsilon_r\mu_r - (\lambda_0/2a)^2\right]^{\frac{1}{2}},$$

where β_d is phase constant of the wave in the dielectric medium having permittivity ε_r, λ_g, the guide wavelength, μ_r, the relative permeability ($\mu_r \approx 1$ at high frequencies), λ_0, the free space wavelength and a, the wider dimension of waveguide.

The dielectric constant of the pure KDP crystal [18] is compared with the standard value and is in agreement with it. It can be noted that the dielectric constant of doped KDP crystal is less than that of the pure KDP crystal which may be due to the decrease of dipole moments of the molecules

able 5. Indexed powder XRD pattern for α - valine doped KDP crystal.

No	h	k	l	d(obs)	d(calc)	Diff. (d)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5 11758	5 09228	0 02530	17 314	17 401	-0 087
2	2	0	0	3.74812	3.73852	0.00960	23.719	23 781	-0 062
3	2	1	1	3 03051	3.01358	0 01693	29 450	29 619	-0 169
4	1	1	2	2.92001	2.90522	0.01479	30.591	30.751	-0 160
5	2	2	0	2 64268	2 64353	-0.00085	33.894	33 882	0 011
6	2	0	2	2 55823	2.54614	0 01209	35 048	35.220	-0 172
7	3	1	0	2.35533	2 36445	-0.00912	38.179	38 026	0 153
8	1	0	3	2.23257	2.21418	0 01839	40.367	40.717	-0 350
9	3	2	1	1 99444	1.98729	0.00715	45.439	45 612	-0.173
10	3	1	2	1 96315	1 95524	0 00791	46 205	46 403	-0 198
11	4	0	0	1.86802	1 86926	-0 00124	48.706	48 672	0.034
12	4	2	0	1 67332	1.67192	0 00140	54.818	54.868	-0 050
13	2	0	4	1.58331	1 57648	0.00683	58 223	58 500	-0 277
14	4	2	2	1 51570	1 50679	0 00891	61.090	61.490	-0 400
15	5	1	0	1 46277	1.46637	-0.00360	63.552	63 378	0 174
16	5	2	1	1 35633	1.36158	-0 00525	69 212	68 907	0 305
17	2	1	5	1 28004	1.28422	-0.00418	73 995	73.714	0 281
18	3	0	5	1 21022	1 21456	-0 00434	79 062	78 724	0 338

ible 6. Indexed powder pattern for α - cystine doped KDP crystal

No	h	k	l	d(obs)	d(calc)	Diff (d)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5 09958	5 08133	0.01825	17 376	17 439	-0 063
2	2	0	0	3 73781	3 71272	0 02509	23 786	23 949	-0 163
3	2	1	1	3 02040	2 99777	0 02263	29 551	29 779	-0.228
4	1	1	2	2 92047	2 90317	0 01730	30 586	30 773	-0 187
5	2	2	0	2.64824	2.62529	0 02295	33.820	34 125	-0 305
6	2	0	2	2 56029	2 54066	0 01963	35 019	35 298	-0.279
7	3	1	0	2 35063	2 34813	0.00250	38 258	38 301	-0 042
8	1	0	3	2 22958	2.21689	0.01269	40.423	40 665	-0.242
9	3	2	1	1.99325	1.97500	0 01825	45.468	45 912	-0.444
10	3	1	2	1 96141	1 94721	0 01420	46 249	46 606	-0.357
11	4	1	1	1 76323	1.74364	0 01959	51 808	52 434	-0 626
12	4	2	0	1.67429	1 66038	0 01391	54 784	55 282	-0 498
13	2	0	4	1.57801	1 57713	0.00088	58 438	58 474	-0 036
14	5	1	0	1 46160	1 45625	0.00535	63 609	63 871	-0 261
15	5	2	1	1.35541	1 35264	0.00277	69 266	69 428	-0.162
16	5	1	2	1 32636	1.34361	-0.01725	71.008	69.962	1.046
17	4	4	0	1.29623	1 31264	-0 01641	72.920	71 865	1 055
18	2	1	5	1 28118	1.28510	-0.00392	73 918	73.655	0.263
19	3	0	5	1 21281	1.21441	-0.00160	78.860	78.736	0 124
20	4	2	4	1 20413	1.20192	0.00221	79 541	79 716	-0.175

admixture, thereby confirming the high dielectric strength of doped KDP crystals.

3.4 Thermal analyses :

The KDP type compounds for different heating cycles show a high temperature phase transition (HTPT) at a characteristic temperature T_p. There are however, large discrepancies found in the literature [19 - 30] concerning the nature of this transition, as well as regarding the number of additional transitions at high temperatures. For example, a structural phase transition from tetragonal to monoclinic symmetry has been proposed for KDP type compounds heated above room temperature, loss of water will take place, as in the following reaction:

$$n\mathrm{MH_2PO_4}(s) \rightarrow \mathrm{M_nH_2P_nO_{3n+1}}(s) + (n-1)\,\mathrm{H_2O}(v),$$
$$(n \geq 1)$$

where n is the number of molecules participating in the thermal composition, s and v denote solid or vapor state, respectively. According to Lee [22], as a consequence of the above equation, the term HTPT at T_p should be replaced by the term, onset of partial polymerization at reaction sites on the surface. Lee concluded that the high temperature phenomena occurring upon heating around T_p in KDP type crystals were due to the thermal dehydration.

The TG studies of the pure and doped KDP crystals are recorded under nitrogen atmosphere from room temperature to 800°C and the results from the thermogram are presented in Table 10. From the TG curve of the pure KDP crystal, it is seen that the crystal is thermally stable up to 300°C in the nitrogen atmosphere and after this temperature, a single stage decomposition takes place. The weight loss is around 12.8% and this corresponds to approximately the loss of one water molecule for every KPO_3 unit and the end residue is large. In the amino acid doped crystals, the starting decomposing temperature is same for all the crystals except for the alanine and valine-doped crystals. In these two crystals, the starting decomposition temperatures are shifted to 328°C and 331°C respectively. The weight losses are slightly decreased to 11.9% in the case of α - histidine and β - alanine doped crystals whereas in the other cases, the weight losses are almost around that of the pure KDP crystal.

Table 7. Indexed powder pattern for β - alanine doped KDP crystal

S No	h	k	l	d(obs)	d(calc)	Diff (d)	2θ (obs)	2θ (calc)	Diff (2θ)
1	1	0	1	5.08861	5 09132	-0 00271	17 413	17 404	0.009
2	2	0	0	3.72346	3 73678	-0 01332	23.879	23 792	0 086
3	2	1	1	3.01561	3.01247	0.00314	29 599	29 631	-0 032
4	1	1	2	2.91538	2 90491	0 01047	30 641	30 754	-0.113
5	2	2	0	2.63976	2 64230	-0.00254	33.932	33.899	0.034
6	2	0	2	2 55847	2 54566	0 01281	35 045	35 227	-0.182
7	3	1	0	2 36187	2 36335	-0.00148	38 069	38.045	0.025
8	3	0	1	2 34592	2.34527	0 00065	38 338	38 349	-0 011
9	1	0	3	2 22433	2 21419	0 01014	40 523	40.717	-0.194
10	3	2	1	1.98565	1.98644	-0.00079	45 652	45 633	0 019
11	3	1	2	1.95874	1 95465	0.00409	46 315	46 418	-0 103
12	2	1	3	1.91476	1 90490	0 00986	47 443	47 704	-0 261
13	4	2	0	1.67998	1.67114	0.00884	54.583	54.896	-0.313
14	2	0	4	1 57552	1 57641	-0 00089	58 539	58.502	0 036
15	3	2	3	1 54751	1.54521	0.00230	59.705	59.803	-0 098
16	5	1	2	1.35149	1 35062	0.00087	69 495	69 547	-0.051
17	5	3	0	1.27799	1 28170	-0 00371	74.133	73 883	0 251
18	3	0	5	1 21086	1 21448	-0 00362	79.012	78 731	0 281
19	4	2	4	1 20332	1 20485	-0 00153	79 605	79 484	0 121

Table 8. Lattice parameters calculated from powder X-ray diffraction pattern

Crystal	a = b (Å)	c(Å)	α = β = γ (in degrees)	Volume of the Unit Cell (Å)³
Pure KDP	7 4519	7.0012	90	389.3358
KDP + α - alanine	7 4641	6 9762	90	388.6677
KDP + α - leucine	7.4594	6 9863	90	388.7397
KDP + α - histidine	7 4653	6 9614	90	387.9690
KDP + α - valine	7.4770	6.9545	90	388.7969
KDP + α - cystine	7.4254	6.9685	90	384.2210
KDP + β - alanine	7.4736	6 9548	90	388 4551

From the DSC analysis of the pure KDP crystal, it is found that there is an endothermic peak at 191°C, which may correspond to the so-called high temperature transition temperature. On heating further, several endothermic peaks are formed at 207, 231, 244, 264 and 272 °C respectively. The change in enthalpy at 231°C is 21.045 J / g. In the alanine doped crystal, the small endothermic peak at 191°C corresponding to the transition temperature of the parent KDP is missing. But there are some endothermic peaks at 225, 250, 278 and 308°C, which are slightly shifted on either side of the corresponding endotherms of pure KDP crystals. The change in enthalpy at 206°C and 225°C are 6.771 and 35.650 J/g respectively. There are large numbers of endotherms in the leucine-doped KDP crystals starting from 193°C.The change in the enthalpy at 221°C is 10.368 J/g. For the histidine-doped crystal, the endothermic peaks appear at 201,236,278 and 293°C and the change in enthalpy at 201°C is 20.215 J / g. In the case of valine-doped crystal, the endotherms are formed at 196,231, 276, 290, 303 and 315°C and the change in enthalpies at 196 and 276 °C are 16.621 and 191.678 J/g respectively. There are only three endotherms in the cystine doped crystal at 200 °C, 251°C and 278°C and the energy liberated at these temperatures are 35.8080, 15.846 and 248.467 J/ g respectively. For the β-alanine doped KDP crystal, the endothermic peaks are formed at 218, 235, 275, 292, 299 and 311 °C and the change in enthalpies are 39.1914 and 76 994 J/g at temperatures 235°C and 275°C respectively. From this study, it is concluded that the amino acid provides a favourable root for crystallization to produce a crystal with much more perfection than the parent. This property may be assumed to arise by the hydrophobic property of the amino acid which facilitates slow and steady crystal growth

Table 9. Dielectric constants of the pure and doped KDP crys 19 403 GHz

Crystal	Thickness (cm)	Dielectric constant
Pure KDP	0.292	5 5717
		5 4716
		5 3745
KDP + α - alanine	0.550	3 7218
		3 6716
		3 6226
		3 5748
KDP + α leucine	0.463	3 4528
		3 4081
		3 3645
KDP + α - histidine	0.260	4 2303
		4 1641
		4 0638
KDP + α - valine	0 404	4 7950
		4 7128
		4 6429
KDP + α - cystine	0.548	3.6716
		3 6226
		3.4822
KDP + β - alanine	0.525	3 9478
		3 8919
		3.8374

Table 10. Thermal analysis of pure and doped KDP crystal

Crystal	Starting temperature of thermal decomposition (°C)	% of weight loss
Pure KDP	300	12.793
KDP + α - alanine	328	12.466
KDP + α - leucine	300	12 748
KDP + α - histidine	300	11 964
KDP + α - valine	331	13 060
KDP + α - cystine	300	12 341
KDP + β - alanine	300	11 912

4. Conclusions

The pure and amino acids-doped potassium dihydrogen phosphate crystals were grown using solution growth technique. The presences of additives are confirmed through XRD patterns and the lattice parameters were evaluated. From the XRD study, it is found that the lattices of the doped crystals are slightly distorted. Also, FTIR and FTRaman study confirms the presence of amino acids in the doped crystal since in the spectra of the doped crystals, some of the main vibrations of amino acids are present. From the dielectric studies of the pure and doped KDP crystals in the microwave region, it is found that the addition of amino acids decreases the dielectric constant of the doped crystals because of the presence of ionic impurities. From the thermal analysis, the different stages of decomposition have been identified and reported. The thermal stability of some of the doped crystals has been increased due to doping of amino acids

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